metal-organic compounds

Redetermination of poly[aquadi-μ_3-oxy-diacetato-dicopper(II)]

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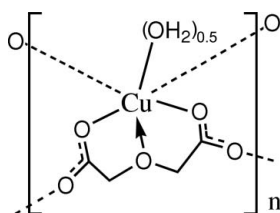
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The title complex, $[Cu_2(C_4H_4O_5)_2(H_2O)]_n$, has a two-dimensional layer structure. The Cu atom has a distorted octahedral (CuO_6) environment and is coordinated by four carboxylate group O atoms from three different oxydiacetate ligands in a planar arrangement and one half-occupancy water molecule and an ether O atom in the axial positions. In the crystal structure, weak intra- and intermolecular O—H···O hydrogen bonds help to stabilize the crystal packing. The structure has already been published [Whitlow & Davey (1975). *J. Chem. Soc. Dalton. Trans*. pp. 1228–1232]; this redetermination reports the structure with higher precision.

Related literature

For related literature, see: Whitlow & Davey (1975).

Experimental

Crystal data

$[Cu_2(C_4H_4O_5)_2(H_2O)]$	Orthorhombic, $Pbcn$
$M_r = 409.24$	$a = 9.2695$ (11) Å
$b = 14.3052$ (2) Å	Mo $K\alpha$ radiation
$c = 9.2715$ (11) Å	$\mu = 3.52$ mm^{-1}
$V = 1229.4$ (2) Å^3	$T = 294$ (2) K
$Z = 4$	$0.16 \times 0.10 \times 0.06$ mm

Data collection

Rigaku Saturn diffractometer	1544 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	1477 independent reflections
$T_{min} = 0.660$, $T_{max} = 0.812$	1385 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	102 parameters
$wR(F^2) = 0.085$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
1477 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O4^i	1.950 (3)	Cu1—O2^{ii}	1.958 (3)
Cu1—O5	1.953 (3)	Cu1—O3	2.498 (3)
Cu1—O1	1.955 (3)	Cu1—O6	2.746 (8)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6B···O5	0.85	2.49	2.909 (8)	112
O6—H6B···O3^{iii}	0.85	2.22	2.996 (11)	152
O6—H6A···O1	0.85	2.05	2.905 (8)	180

Symmetry code: (iii) $-x + \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2052).

References

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

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Rigaku/MSC (2005). *CrystalClear*. Version 1.3.6. Rigaku/MSC, The Woodlands, Texas, USA.

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supplementary materials

Redetermination of poly[aquadi-μ_3-oxydiacetato-dicopper(II)]

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Comment

The structure of the title complex, (I), was determined some years ago [Whitlow & Davey, 1975)] using diffraction data collected at ambient temperature, the determination gave higher *R* values (*R* =0.088) and *Z*=8. The information of the structure was not found at the database of CCDC. Complex, (I), has been obtained as a by-product of study of heterobimetallic complexes involving $Ba(NO_3)_2$, $Cu(NO_3)_2$ and oxydiacetic acid, using Na_2CO_3 as base. We have taken this opportunity to redetermine the structure of (I) at 294 (2) K, leading to significantly improved precision.

The asymmetric unit in the structure of (I) comprises one Cu atom, one complete oxydiacetate dianion and half a water molecule, and is shown in Fig. 1 in a symmetry-expanded view, which displays the full coordination of the Cu atom. Selected geometric parameters are given in Table 1. The Cu atom has octahedral coordination, with O1, O5, O2[ii] and O4[i] of three nonequivalent oxydiacetate dianions in a planar arrangement, and O3 and O6 atoms from one ether oxygen and half a water molecules in a *trans* conformation. Thus, the coordination octahedra of the Cu atoms can be visualized as having an elongated axial distortion.

In the structure of (I), each Cu atom is bonded to an oxydiacetate ligand *via* the O1 and O5 atoms of carboxylate groups and the ether oxygen O3 atom, each oxydiacetate ligand connect with other two Cu atoms *via* the O2 and O4 atom as a monodentate bonding mode and a bridging bonding mode, respectively. These result in the Cu1···Cu1 separations are 4.8666 (9)Å and 4.8501 (10) Å, respectively, and complete a two-dimensional layer connectivity of the structure parallel to *ac* plane. A number of weak intra- and intermolecular O–H···O hydrogen bonds interactions (see Table 2) further stabilize the two-dimensional framework within this layer. A packing diagram for the structure of (I) is shown in Fig. 2.

Experimental

A mixture of 20 ml aqueous solution of sodium carbonate anhydrous (0.43 g, 4 mmol) and oxydiacetic acid (0.54 g, 4.0 mmol) was added dropwise into a solution of cupric nitrate (0.49 g, 2 mmol) and barium nitrate (0.52 g, 2 mmol) in 20 ml of distillated water under stirring at the room temperature for 20 min. After filtration, slow evaporation the filtrate over a period of two week at room temperature provided the crystals of (I).

Refinement

The H atoms of the water molecule were found in difference Fourier maps and during refinement were fixed at an O–H distance of 0.85 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(O)$. The H atoms of C–H groups were placed geometrically and during refinement were treated using a riding model, with C–H = 0.97 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C)$.
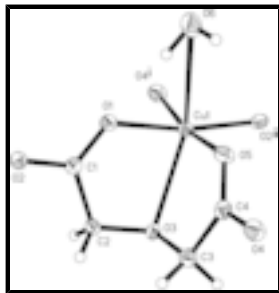
supplementary materials

Figures

Fig. 1. A view of the structure of (I), showing the atom-numbering Scheme; displacement ellipsoids were drawn at the 30% probability level. Symmetry codes (i) $-x + 3/2$, $-y + 1/2$, $z + 1/2$; (ii) $x + 1/2$, $-y + 1/2$, $-z + 1$.
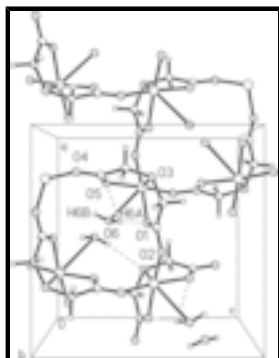

Fig. 2. Packing diagram showing hydrogen bonds interactions, viewed down the *b* axis.

poly[aquadi-µ₃-oxydiacetato-dicopper(II)]

Crystal data

$[Cu_2(C_4H_4O_5)_2(H_2O)]$	$F_{000} = 816$
$M_r = 409.24$	$D_x = 2.211$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo *Kα* radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 1544 reflections
$a = 9.2695$ (11) Å	$\theta = 2.6–27.9°$
$b = 14.3052$ (2) Å	$\mu = 3.52$ mm^{-1}
$c = 9.2715$ (11) Å	$T = 294$ (2) K
$V = 1229.4$ (2) Å^3	Plate, blue
$Z = 4$	$0.16 \times 0.10 \times 0.06$ mm

Data collection

Rigaku Saturn diffractometer	1477 independent reflections
Radiation source: fine-focus sealed tube	1385 reflections with $I > 2\sigma(I)$
Monochromator: confocal	$R_{int} = 0.013$
Detector resolution: 28.5714 pixels mm^{-1}	$\theta_{max} = 27.9°$
$T = 294(2)$ K	$\theta_{min} = 1.4°$
ω scans	$h = -1 \rightarrow 12$
Absorption correction: multi-scan	$k = -3 \rightarrow 18$

(Jacobson, 1998)

$T_{min} = 0.660$, $T_{max} = 0.812$

$l = -1 \rightarrow 12$

1544 measured reflections

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o{}^2) + (0.0397P)^2 + 0.8539P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
1477 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}
102 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0116 (11)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Cu1	0.72930 (5)	0.20200 (3)	0.46964 (6)	0.02384 (17)	
O1	0.5403 (3)	0.2600 (2)	0.4973 (5)	0.0304 (8)	
O2	0.3991 (3)	0.3753 (2)	0.5700 (4)	0.0287 (7)	
O3	0.7808 (3)	0.37024 (17)	0.5203 (3)	0.0227 (5)	
O4	0.8062 (4)	0.3780 (3)	0.1361 (3)	0.0314 (7)	
O5	0.7509 (4)	0.2607 (3)	0.2807 (4)	0.0293 (8)	
C1	0.5227 (4)	0.3416 (3)	0.5428 (5)	0.0227 (9)	
C2	0.6489 (4)	0.4050 (3)	0.5749 (5)	0.0245 (9)	
H2A	0.6305	0.4661	0.5332	0.029*	
H2B	0.6572	0.4128	0.6785	0.029*	
C3	0.8234 (5)	0.4079 (3)	0.3855 (5)	0.0301 (11)	
H3A	0.9263	0.4200	0.3874	0.036*	
H3B	0.7746	0.4672	0.3709	0.036*	

C4	0.7895 (5)	0.3437 (3)	0.2599 (5)	0.0242 (9)	
O6	0.5441 (8)	0.1079 (4)	0.2898 (10)	0.0489 (19)	0.50
H6A	0.5427	0.1526	0.3503	0.059*	0.50
H6B	0.5810	0.1331	0.2154	0.059*	0.50

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0263 (3)	0.0194 (2)	0.0258 (3)	0.0012 (2)	0.00097 (18)	−0.0001 (3)
O1	0.0215 (14)	0.0259 (19)	0.044 (2)	−0.0007 (11)	−0.0010 (19)	−0.0069 (15)
O2	0.0237 (15)	0.0221 (17)	0.040 (2)	0.0032 (12)	0.0019 (12)	0.0019 (15)
O3	0.0205 (12)	0.0265 (13)	0.0212 (14)	0.0001 (10)	0.0026 (10)	−0.0004 (12)
O4	0.0426 (18)	0.0308 (19)	0.0207 (16)	−0.0011 (15)	0.0001 (13)	−0.0009 (13)
O5	0.0404 (18)	0.0229 (19)	0.0246 (14)	−0.0042 (13)	−0.0009 (17)	−0.0016 (13)
C1	0.023 (2)	0.024 (2)	0.022 (2)	0.0011 (16)	−0.0022 (15)	0.006 (2)
C2	0.025 (2)	0.022 (2)	0.026 (3)	0.0014 (16)	0.0015 (16)	−0.0053 (18)
C3	0.034 (2)	0.030 (2)	0.026 (3)	−0.0036 (19)	0.003 (2)	0.0000 (18)
C4	0.020 (2)	0.028 (2)	0.025 (2)	0.0027 (18)	−0.0024 (16)	−0.0006 (17)
O6	0.055 (6)	0.027 (3)	0.064 (7)	0.005 (3)	0.021 (3)	0.003 (4)

Geometric parameters (Å, °)

Cu1—O4^i	1.950 (3)	O4—Cu1^{iv}	1.950 (3)
Cu1—O5	1.953 (3)	O5—C4	1.255 (5)
Cu1—O1	1.955 (3)	C1—C2	1.510 (6)
Cu1—O2^{ii}	1.958 (3)	C2—H2A	0.9700
Cu1—O3	2.498 (3)	C2—H2B	0.9700
Cu1—O6	2.746 (8)	C3—C4	1.516 (6)
O1—C1	1.252 (5)	C3—H3A	0.9700
O2—C1	1.268 (5)	C3—H3B	0.9700
O2—Cu1^{iii}	1.958 (3)	O6—O6^v	1.101 (13)
O3—C2	1.414 (4)	O6—H6A	0.8504
O3—C3	1.417 (5)	O6—H6B	0.8505
O4—C4	1.258 (5)		
O4^i—Cu1—O5	168.50 (15)	O3—C2—H2A	109.0
O4^i—Cu1—O1	89.68 (15)	C1—C2—H2A	109.0
O5—Cu1—O1	91.52 (11)	O3—C2—H2B	109.0
O4^i—Cu1—O2^{ii}	87.29 (12)	C1—C2—H2B	109.0
O5—Cu1—O2^{ii}	89.56 (14)	H2A—C2—H2B	107.8
O1—Cu1—O2^{ii}	169.87 (14)	O3—C3—C4	112.9 (4)
O3—Cu1—O6	134.91 (15)	O3—C3—H3A	109.0
O1—Cu1—O3	74.80 (11)	C4—C3—H3A	109.0
O1—Cu1—O6	74.19 (19)	O3—C3—H3B	109.0
C1—O1—Cu1	123.9 (3)	C4—C3—H3B	109.0
C1—O2—Cu1^{iii}	118.4 (3)	H3A—C3—H3B	107.8
C2—O3—C3	115.0 (3)	O5—C4—O4	123.0 (4)
C4—O4—Cu1^{iv}	118.2 (3)	O5—C4—C3	121.0 (4)

C4—O5—Cu1	125.0 (3)	O4—C4—C3	116.1 (4)
O1—C1—O2	122.6 (4)	O6^v—O6—H6A	115.5
O1—C1—C2	121.7 (4)	O6^v—O6—H6B	75.8
O2—C1—C2	115.6 (4)	H6A—O6—H6B	102.9
O3—C2—C1	112.8 (3)		
O4^i—Cu1—O1—C1	108.4 (4)	C3—O3—C2—C1	97.3 (4)
O5—Cu1—O1—C1	−83.1 (4)	O1—C1—C2—O3	12.5 (7)
O2^{ii}—Cu1—O1—C1	−179.1 (7)	O2—C1—C2—O3	−170.0 (4)
O4^i—Cu1—O5—C4	176.0 (6)	C2—O3—C3—C4	−100.0 (4)
O1—Cu1—O5—C4	80.1 (4)	Cu1—O5—C4—O4	177.8 (3)
O2^{ii}—Cu1—O5—C4	−110.0 (4)	Cu1—O5—C4—C3	−0.3 (7)
Cu1—O1—C1—O2	−174.6 (3)	Cu1^{iv}—O4—C4—O5	−0.2 (6)
Cu1—O1—C1—C2	2.7 (7)	Cu1^{iv}—O4—C4—C3	178.0 (3)
Cu1^{iii}—O2—C1—O1	−2.9 (7)	O3—C3—C4—O5	−11.2 (6)
Cu1^{iii}—O2—C1—C2	179.6 (3)	O3—C3—C4—O4	170.6 (4)

Symmetry codes: (i) −x+3/2, −y+1/2, z+1/2; (ii) x+1/2, −y+1/2, −z+1; (iii) x−1/2, −y+1/2, −z+1; (iv) −x+3/2, −y+1/2, z−1/2; (v) −x+1, y, −z+1/2.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6B···O5	0.85	2.49	2.909 (8)	112
O6—H6B···O3^{iv}	0.85	2.22	2.996 (11)	152
O6—H6A···O1	0.85	2.05	2.905 (8)	180

Symmetry codes: (iv) −x+3/2, −y+1/2, z−1/2.

Fig. 1

Fig. 2